Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Bis(pyridin-2-ylmethyl)ammonium nitrate

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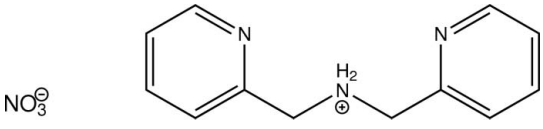
Received 26 March 2013; accepted 28 March 2013

Key indicators: single-crystal X-ray study; T = 200 K; mean σ(C–C) = 0.002 Å; R factor = 0.041; wR factor = 0.122; data-to-parameter ratio = 17.1.

In the title compound, $C_{12}H_{14}N_3^+\cdot NO_3^-$, the mononitrate of protonated bis(pyridin-2-ylmethyl)amine, the least-squares planes defined by the non-H atoms of the two aromatic moieties intersect at an angle of 7.91 (6)°. In the crystal, N—H···N, N—H···O and C—H···N hydrogen bonds, as well as C—H···O contacts, connect the entities into a three-dimensional network. The shortest centroid–centroid distance between two aromatic systems is 3.7255 (8) Å and is apparent between the two different aromatic moieties.

Related literature

For the crystal structure of the trinitrate of bis(pyridin-2-ylmethyl)amine, see: Junk *et al.* (2006). For graph-set analysis of hydrogen bonds, see: Etter *et al.* (1990); Bernstein *et al.* (1995).



Experimental

Crystal data

$C_{12}H_{14}N_3^+\cdot NO_3^-$
M_r = 262.27
Orthorhombic, *Pbca*
a = 11.2236 (2) Å
b = 13.4714 (4) Å
c = 16.5303 (4) Å
V = 2499.34 (11) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 200 K
0.50 × 0.35 × 0.24 mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
T_{min} = 0.923, T_{max} = 1.000
12816 measured reflections
3082 independent reflections
2568 reflections with $I > 2\sigma(I)$
R_{int} = 0.014

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.122
S = 1.04
3082 reflections
180 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C13—H13···N2	0.95	2.61	3.5339 (18)	164
N1—H71···O3^{i}	0.893 (18)	2.349 (18)	3.0721 (15)	138.2 (14)
N1—H72···O2^{ii}	0.902 (19)	1.982 (19)	2.8831 (15)	176.1 (15)
N1—H72···O1^{ii}	0.902 (19)	2.584 (18)	3.2201 (16)	128.1 (14)
N1—H72···N2^{ii}	0.902 (19)	2.651 (18)	3.4905 (15)	155.1 (14)
C15—H15···O2^{iii}	0.95	2.39	3.1858 (19)	141
C1—H1*A*···O1^{iv}	0.99	2.54	3.5132 (18)	167
C25—H25···O1^{v}	0.95	2.53	3.3959 (16)	151
C24—H24···O2^{vi}	0.95	2.55	3.4620 (16)	161

Symmetry codes: (i) $x, -y+\frac{1}{2}, z+\frac{1}{2}$; (ii) $-x+\frac{3}{2}, -y, z+\frac{1}{2}$; (iii) $x-\frac{1}{2}, y, -z+\frac{1}{2}$; (iv) $x+\frac{1}{2}, y, -z+\frac{1}{2}$; (v) $-x+1, -y, -z+1$; (vi) $x, y, z+1$.

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2009).

The authors thank NMMU for the allocation of research facilities.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: VN2068).

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supplementary materials

Acta Cryst. (2013). E**69**, o661 [doi:10.1107/S1600536813008593]

Bis(pyridin-2-ylmethyl)ammonium nitrate

Abubak'r Abrahams, Bernardus van Brecht and Richard Betz

Comment

Upon the attempted synthesis of a rare-earth metal coordination compound applying bis(pyridin-2-ylmethyl)amine as an auxilliary ligand, the title compound was unintentionally obtained as the only crystalline reaction product. The crystal structure of the trinitrate salt of bis(pyridin-2-ylmethyl)amine has been reported earlier (Junk *et al.*, 2006).

The twofold-protonated amine-type nitrogen atom is present in a tetrahedral coordination environment. The angles set up by the atoms connected to it cover a range of 107.7 (11)–111.81 (9) °. The least-squares planes defined by the respective non-hydrogen atoms of the two aromatic moieties enclose an angle of 7.91 (6) ° (Fig. 1).

In the crystal, classical hydrogen bonds of the N–H···O type are observed next to C–H···O contacts whose range falls by more than 0.1 Å below the sum of van-der-Waals radii of the atoms participating. In addition, a C–H···N contact involving the nitrate anion is apparent. One of the N–H···O hydrogen bonds shows bifurcation. All the aforementioned contacts are exclusively established between atoms on the cation as well as the anion. Metrical parameters as well as information about the symmetry of these contacts are summarized in Table 1. In total, the entities of the crystal structure are connected to a three-dimensional network. In terms of graph-set analysis (Etter *et al.*, 1990; Bernstein *et al.*, 1995), the descriptor for the C–H···O contacts is *DDDD* on the unary level while the classical hydrogen bonds necessitate a *DDD* descriptor on the same level if the bifurcated hydrogen bond is counted as two separate hydrogen bonds. The shortest intercentroid distance between two aromatic systems is measured at 3.7255 (8) Å and is apparent between the two different aromatic moieties (Fig. 2).

The packing of the title compound in the crystal structure is shown in Figure 3.

Experimental

Lanthanum nitrate was reacted with bis(pyridin-2-ylmethyl)amine in water. Upon free evaporation of the solvent, a crystalline solid was obtained from which irregular-shaped white crystals could be selected.

Refinement

Carbon-bound H atoms were placed in calculated positions (C–H 0.95 Å for aromatic carbon atoms and C–H 0.99 Å for methylene groups) and were included in the refinement in the riding model approximation, with U(H) set to 1.2U_{eq}(C). Both nitrogen-bound H atoms were located on a difference Fourier map and refined freely.

Computing details

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT* (Bruker, 2007); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and Mercury (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008) and *PLATON* (Spek, 2009).

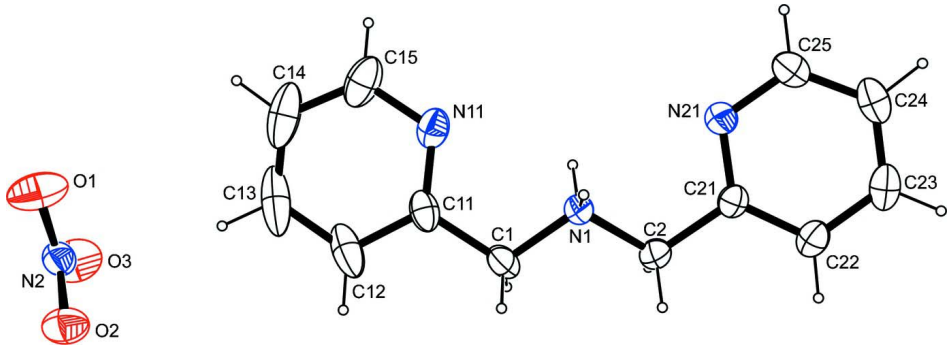

Figure 1

The molecular structure of the title compound, with atom labels and anisotropic displacement ellipsoids (drawn at 50% probability level).

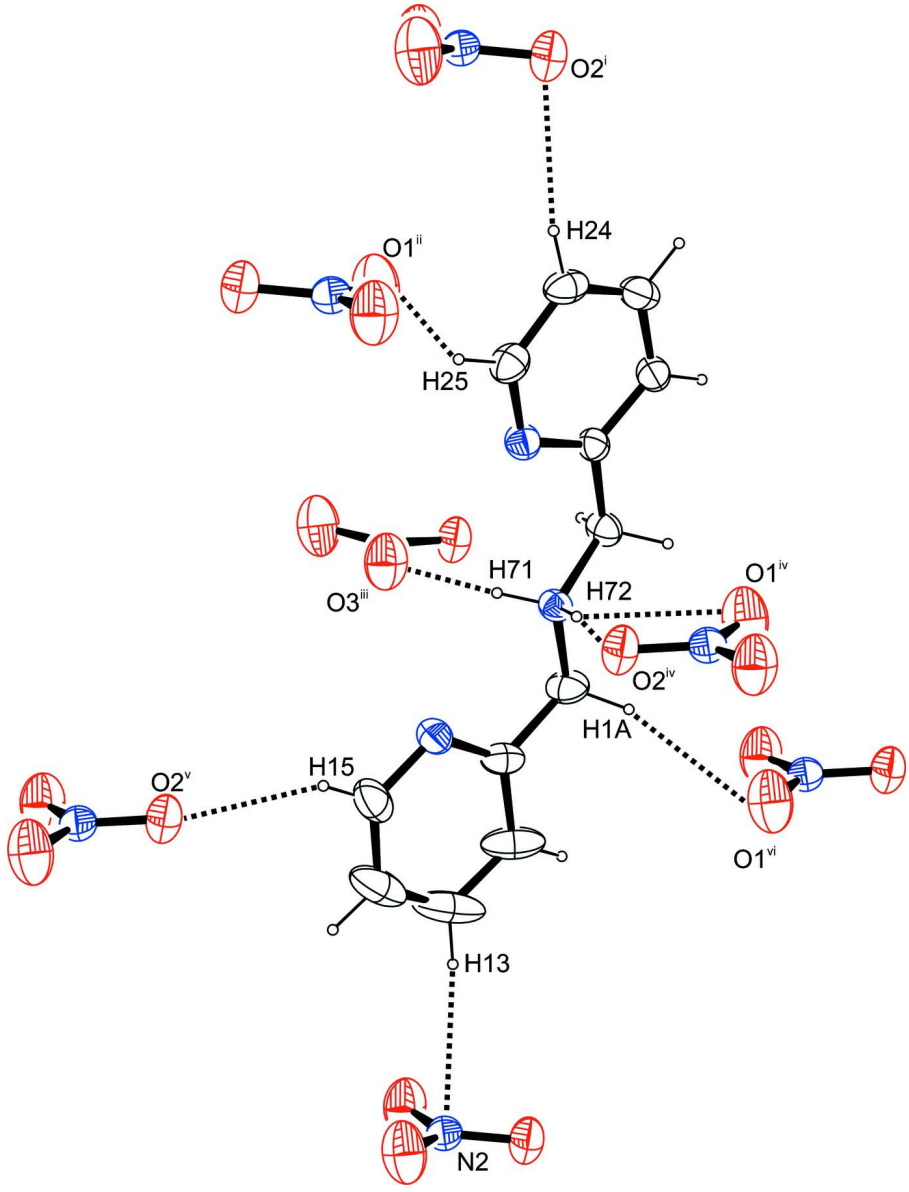

Figure 2

Intermolecular contacts, viewed approximately along [1 1 0]. Symmetry operators: [i] *x*, *y*, *z* + 1; [ii] -*x* + 1, -*y*, -*z* + 1; [iii] *x*, -*y* + 1/2, *z* + 1/2; [iv] -*x* + 3/2, -*y*, *z* + 1/2; [v] *x* - 1/2, *y*, -*z* + 1/2; [vi] *x* + 1/2, *y*, -*z* + 1/2.

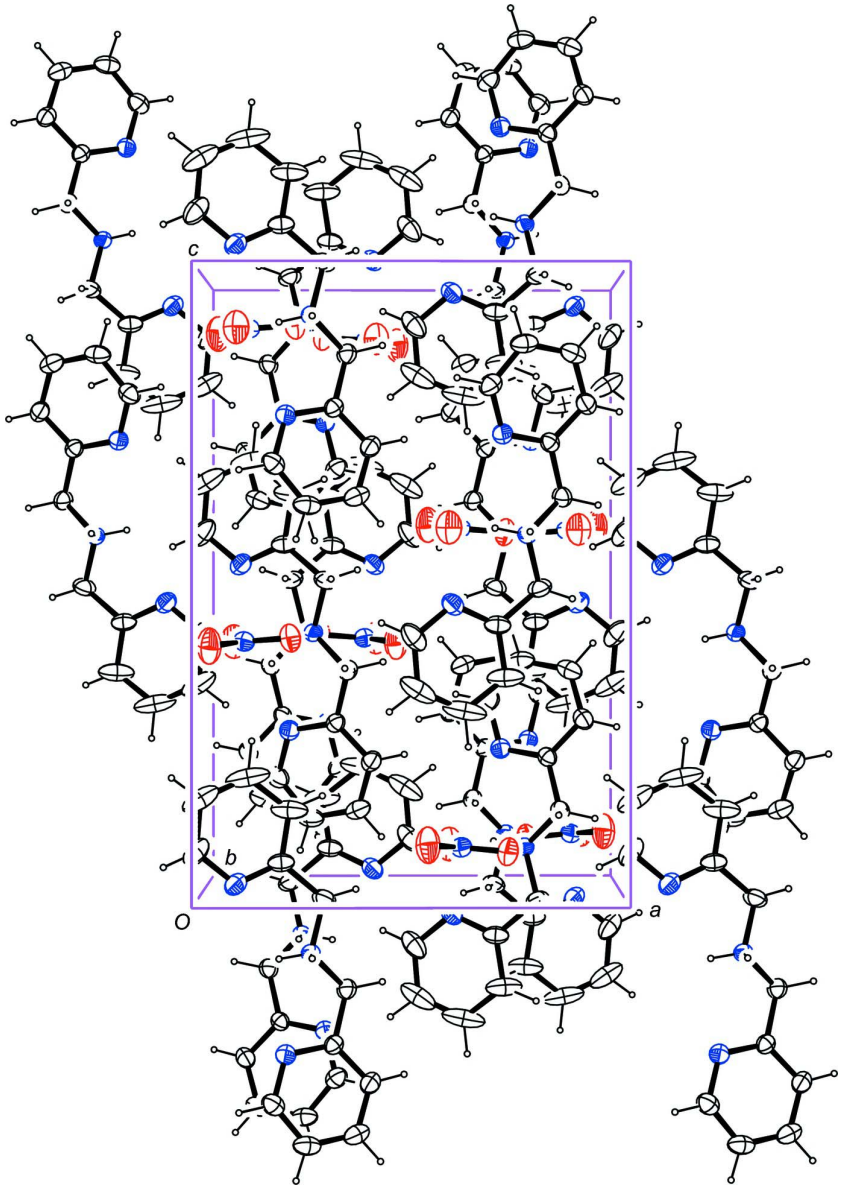

Figure 3

Molecular packing of the title compound, viewed along [0 1 0] (anisotropic displacement ellipsoids drawn at 50% probability level).

Bis(pyridin-2-ylmethyl)ammonium nitrate

Crystal data

$C_{12}H_{14}N_3^+ \cdot NO_3^-$
$M_r = 262.27$
Orthorhombic, *Pbca*
Hall symbol: -P 2ac 2ab
$a = 11.2236\ (2)$ Å
$b = 13.4714\ (4)$ Å
$c = 16.5303\ (4)$ Å
$V = 2499.34\ (11)$ Å^3
$Z = 8$
$F(000) = 1104$
$D_x = 1.394$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 5628 reflections
$\theta = 2.5$–$28.2°$
$\mu = 0.10$ mm^{-1}
$T = 200$ K
Irregular, white
0.50 × 0.35 × 0.24 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
T_{min} = 0.923, T_{max} = 1.000
12816 measured reflections
3082 independent reflections
2568 reflections with $I > 2\sigma(I)$
R_{int} = 0.014
θ_{max} = 28.3°, θ_{min} = 2.7°
h = −8→14
k = −17→17
l = −22→17

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.122
S = 1.04
3082 reflections
180 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0695P)^2 + 0.627P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.53822 (10)	0.03915 (9)	0.09542 (8)	0.0595 (3)
O2	0.72195 (8)	0.07826 (8)	0.08342 (6)	0.0438 (3)
O3	0.58787 (10)	0.19315 (8)	0.09035 (8)	0.0540 (3)
N1	0.76754 (9)	0.13548 (8)	0.57810 (6)	0.0257 (2)
H71	0.6936 (16)	0.1564 (13)	0.5883 (10)	0.044 (4)*
H72	0.7725 (15)	0.0688 (14)	0.5820 (10)	0.044 (4)*
N2	0.61491 (9)	0.10403 (8)	0.08911 (6)	0.0300 (2)
N11	0.59551 (10)	0.11038 (8)	0.46858 (6)	0.0345 (2)
N21	0.71063 (9)	0.11508 (7)	0.73540 (6)	0.0297 (2)
C1	0.79740 (12)	0.16440 (10)	0.49410 (7)	0.0351 (3)
H1A	0.8717	0.1305	0.4774	0.042*
H1B	0.8116	0.2369	0.4919	0.042*
C2	0.84972 (10)	0.18126 (9)	0.63756 (7)	0.0295 (2)
H2A	0.8442	0.2544	0.6335	0.035*
H2B	0.9326	0.1617	0.6246	0.035*
C11	0.69911 (12)	0.13770 (8)	0.43630 (7)	0.0313 (3)
C12	0.71806 (18)	0.14422 (10)	0.35348 (8)	0.0507 (4)
H12	0.7937	0.1623	0.3324	0.061*
C13	0.6227 (2)	0.12345 (11)	0.30224 (9)	0.0657 (6)
H13	0.6315	0.1291	0.2453	0.079*
C14	0.51552 (19)	0.09468 (12)	0.33522 (11)	0.0598 (5)
H14	0.4496	0.0794	0.3014	0.072*
C15	0.50553 (14)	0.08849 (11)	0.41766 (10)	0.0472 (4)
H15	0.4316	0.0678	0.4400	0.057*
C21	0.82056 (10)	0.14965 (8)	0.72268 (7)	0.0255 (2)

C22	0.90516 (11)	0.16031 (9)	0.78369 (7)	0.0309 (3)
H22	0.9828	0.1843	0.7719	0.037*
C23	0.87333 (12)	0.13503 (9)	0.86208 (7)	0.0359 (3)
H23	0.9287	0.1417	0.9052	0.043*
C24	0.75986 (13)	0.10001 (9)	0.87633 (7)	0.0366 (3)
H24	0.7353	0.0829	0.9295	0.044*
C25	0.68233 (11)	0.09025 (9)	0.81153 (7)	0.0346 (3)
H25	0.6049	0.0646	0.8216	0.041*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0397 (6)	0.0467 (6)	0.0920 (9)	−0.0119 (5)	−0.0001 (5)	0.0126 (6)
O2	0.0298 (5)	0.0473 (6)	0.0542 (6)	0.0045 (4)	0.0046 (4)	−0.0013 (4)
O3	0.0484 (6)	0.0330 (5)	0.0805 (8)	0.0060 (4)	−0.0001 (5)	0.0027 (5)
N1	0.0254 (5)	0.0290 (5)	0.0229 (4)	−0.0029 (4)	−0.0008 (3)	0.0030 (3)
N2	0.0309 (5)	0.0333 (5)	0.0260 (5)	0.0003 (4)	0.0013 (4)	0.0017 (4)
N11	0.0339 (5)	0.0374 (5)	0.0322 (5)	0.0069 (4)	−0.0073 (4)	−0.0051 (4)
N21	0.0281 (5)	0.0325 (5)	0.0284 (5)	−0.0005 (4)	0.0000 (4)	0.0034 (4)
C1	0.0395 (6)	0.0421 (6)	0.0236 (5)	−0.0092 (5)	0.0062 (5)	0.0033 (5)
C2	0.0270 (5)	0.0327 (6)	0.0287 (6)	−0.0068 (4)	−0.0022 (4)	0.0014 (4)
C11	0.0494 (7)	0.0219 (5)	0.0225 (5)	0.0018 (5)	−0.0017 (5)	0.0013 (4)
C12	0.0989 (13)	0.0300 (6)	0.0233 (6)	−0.0127 (7)	0.0039 (7)	0.0010 (5)
C13	0.138 (2)	0.0328 (7)	0.0259 (7)	0.0027 (9)	−0.0235 (9)	−0.0003 (5)
C14	0.0905 (14)	0.0376 (7)	0.0513 (9)	0.0206 (8)	−0.0415 (9)	−0.0113 (7)
C15	0.0444 (8)	0.0432 (7)	0.0542 (9)	0.0160 (6)	−0.0214 (6)	−0.0127 (6)
C21	0.0259 (5)	0.0244 (5)	0.0263 (5)	0.0028 (4)	−0.0025 (4)	−0.0014 (4)
C22	0.0289 (5)	0.0323 (6)	0.0316 (6)	0.0044 (4)	−0.0048 (4)	−0.0051 (4)
C23	0.0464 (7)	0.0334 (6)	0.0278 (6)	0.0122 (5)	−0.0096 (5)	−0.0052 (5)
C24	0.0546 (8)	0.0303 (6)	0.0248 (5)	0.0119 (5)	0.0031 (5)	0.0020 (4)
C25	0.0367 (7)	0.0339 (6)	0.0332 (6)	0.0018 (5)	0.0063 (5)	0.0047 (5)

Geometric parameters (Å, º)

O1—N2	1.2311 (15)	C11—C12	1.3883 (17)
O2—N2	1.2541 (14)	C12—C13	1.393 (3)
O3—N2	1.2385 (14)	C12—H12	0.9500
N1—C1	1.4806 (14)	C13—C14	1.376 (3)
N1—C2	1.4822 (14)	C13—H13	0.9500
N1—H71	0.893 (18)	C14—C15	1.370 (2)
N1—H72	0.902 (19)	C14—H14	0.9500
N11—C11	1.3313 (17)	C15—H15	0.9500
N11—C15	1.3473 (17)	C21—C22	1.3926 (15)
N21—C21	1.3354 (15)	C22—C23	1.3866 (18)
N21—C25	1.3403 (15)	C22—H22	0.9500
C1—C11	1.5030 (18)	C23—C24	1.378 (2)
C1—H1A	0.9900	C23—H23	0.9500
C1—H1B	0.9900	C24—C25	1.3864 (19)
C2—C21	1.5061 (16)	C24—H24	0.9500
C2—H2A	0.9900	C25—H25	0.9500

C2—H2B	0.9900		
C1—N1—C2	111.81 (9)	C11—C12—H12	121.0
C1—N1—H71	107.7 (11)	C13—C12—H12	121.0
C2—N1—H71	108.8 (11)	C14—C13—C12	119.15 (15)
C1—N1—H72	108.4 (10)	C14—C13—H13	120.4
C2—N1—H72	109.1 (10)	C12—C13—H13	120.4
H71—N1—H72	111.0 (15)	C15—C14—C13	118.86 (15)
O1—N2—O3	121.03 (11)	C15—C14—H14	120.6
O1—N2—O2	118.66 (11)	C13—C14—H14	120.6
O3—N2—O2	120.29 (11)	N11—C15—C14	123.15 (17)
C11—N11—C15	117.70 (13)	N11—C15—H15	118.4
C21—N21—C25	116.99 (10)	C14—C15—H15	118.4
N1—C1—C11	111.53 (10)	N21—C21—C22	123.50 (11)
N1—C1—H1A	109.3	N21—C21—C2	116.51 (10)
C11—C1—H1A	109.3	C22—C21—C2	119.95 (10)
N1—C1—H1B	109.3	C23—C22—C21	118.41 (12)
C11—C1—H1B	109.3	C23—C22—H22	120.8
H1A—C1—H1B	108.0	C21—C22—H22	120.8
N1—C2—C21	111.51 (9)	C24—C23—C22	118.81 (11)
N1—C2—H2A	109.3	C24—C23—H23	120.6
C21—C2—H2A	109.3	C22—C23—H23	120.6
N1—C2—H2B	109.3	C23—C24—C25	118.70 (11)
C21—C2—H2B	109.3	C23—C24—H24	120.6
H2A—C2—H2B	108.0	C25—C24—H24	120.6
N11—C11—C12	123.13 (13)	N21—C25—C24	123.58 (12)
N11—C11—C1	116.90 (10)	N21—C25—H25	118.2
C12—C11—C1	119.95 (13)	C24—C25—H25	118.2
C11—C12—C13	117.98 (17)		
C2—N1—C1—C11	−166.97 (10)	C13—C14—C15—N11	0.8 (2)
C1—N1—C2—C21	−178.69 (10)	C25—N21—C21—C22	0.28 (17)
C15—N11—C11—C12	−0.18 (18)	C25—N21—C21—C2	−177.56 (10)
C15—N11—C11—C1	178.44 (11)	N1—C2—C21—N21	−20.60 (14)
N1—C1—C11—N11	11.67 (16)	N1—C2—C21—C22	161.48 (10)
N1—C1—C11—C12	−169.68 (11)	N21—C21—C22—C23	−0.91 (17)
N11—C11—C12—C13	1.7 (2)	C2—C21—C22—C23	176.87 (10)
C1—C11—C12—C13	−176.91 (12)	C21—C22—C23—C24	0.33 (17)
C11—C12—C13—C14	−1.9 (2)	C22—C23—C24—C25	0.79 (17)
C12—C13—C14—C15	0.8 (2)	C21—N21—C25—C24	0.94 (18)
C11—N11—C15—C14	−1.1 (2)	C23—C24—C25—N21	−1.49 (19)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C13—H13···N2	0.95	2.61	3.5339 (18)	164
N1—H71···O3^{i}	0.893 (18)	2.349 (18)	3.0721 (15)	138.2 (14)
N1—H72···O2^{ii}	0.902 (19)	1.982 (19)	2.8831 (15)	176.1 (15)
N1—H72···O1^{ii}	0.902 (19)	2.584 (18)	3.2201 (16)	128.1 (14)

N1—H72···N2^{ii}	0.902 (19)	2.651 (18)	3.4905 (15)	155.1 (14)
C15—H15···O2^{iii}	0.95	2.39	3.1858 (19)	141
C1—H1*A*···O1^{iv}	0.99	2.54	3.5132 (18)	167
C25—H25···O1^{v}	0.95	2.53	3.3959 (16)	151
C24—H24···O2^{vi}	0.95	2.55	3.4620 (16)	161

Symmetry codes: (i) x, $-y+1/2$, $z+1/2$; (ii) $-x+3/2$, $-y$, $z+1/2$; (iii) $x-1/2$, y, $-z+1/2$; (iv) $x+1/2$, y, $-z+1/2$; (v) $-x+1$, $-y$, $-z+1$; (vi) x, y, $z+1$.